(12) # EUROPEAN PATENT APPLICATION

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(54) Faom structure of coalesced foam strands of profiles.

(57) Improved closed cell foams, particularly suitable for use in packaging applications, comprise a plurality of coalesced parallel strands or profiles of thermoplastic resin. When the resin is a non-aromatic olefin, the heat seal strength of a film thereof is at least 30 Newtons/inch (2.5 cm) width. Preferably, the resin is a mixture of an olefin polymer resin and a copolymer of ethylene with one or more copolymerizable comonomers having a lower melting point than the olefin polymer resin. The cross-section of the strands or profiles and/or their spacial arrangement advantageously are such that they are joined at their extremities to form a network defining voids. The resin may contain up to 50 weight percent of a nucleating agent, preferably carbon black. The strands and profiles suitably are extruded through a multi-orificed die in which some orifices are temporarily blocked off to produced the desired structural shape.

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Description

FOAM STRUCTURE OF COALESCED FOAM STRANDS OR PROFILES

Background of the Invention

The present invention relates to foamed products. More particularly, the present invention relates to unique foam products which, in at least some embodiments, have exceptionally good cushioning properties at low static loadings and low densities. More particularly, the present invention relates to such a foam comprising a plurality of coalesced distinguishable expanded strands or profiles.

Foamed objects comprising a plurality of coalesced distinguishable expanded strands of foamed polymers (strand foams) have been previously disclosed in U.S. Patent 3,573,152. The foam objects are prepared by extruding a foamable thermoplastic material through a multi-orifice die plate, whereby the individual foamable elements of the strand are formed, expanded and coalesced upon emerging from the die orifices. The exemplified strands are of circular cross-section but there is a reference to the production of strands using multi-orificed dies in which the orifices can be slots squares, holes or special shapes. The advantages of providing the multi-strand product are specified to be (a) superior strength in the plane transverse to the direction of extrusion; (b) extrusion to a predetermined shape without any need to trim; (c) low density product having distinguishable coalesced cellular strands; and (d) ease of change of shape by varying design of the extrusion die. Although there are small voids formed between adjacent strands in the exemplified structures, there is no recognition of any advantage in maximizing or enlarging the volume of said voids from those resulting from close packing of the strands. Further, although the previously mentioned U.S. Patent 3,573,152 discloses that polyethylene resins may be appropriately employed in the preparation of strand foams according to the teachings therein contained, despite diligent efforts by the present inventors, no polyethylene strand foam has been successfully prepared following the teachings of such references.

Shaped closed cell foams are responsive to the needs of a specific application and can be produced in intricate shapes by a continuous process.

One area in which shaped closed cell foams are widely employed is in the field of packaging in order to provide cushion properties. Fragile objects intended to be transported may be encased and supported in a shaped closed cell foamed cushion adapted to conform to the external shape of the object for which protection is desired. Another area is that of seat cushions. A homogeneous shaped closed cell foam having a soft surface layer of a low density foam and a shock absorbing inner layer of a higher desnity foam is desirable for such an application.

Presently known polyethylene foam cushion materials possess propertics adapted to provide particular cushioning performance. For example, higher density foams are suitably employed to achieve peak deceleration forces between about 40 or 50 G's (the gravitational constant) (400 and 500 m/s²) at static loadings of between about 0.5 and 1.5 pounds per square inch (3.5 - 10.5 kPa) in standard 24 inch (61 cm) drop tests. At reduced static loadings, between about 0.1 and about 0.5 pounds per square inch (0.5 - 3.5 kPa), lower density foams on the order of about 1.2 to about 1.8 pounds per cubic foot (1.9 - 2.9 kg/m³) may be employed. However, suitable cushioning, i.e. peak deceleration forces less than about 50 G's (500 m/s²) are not obtainable except upon the use of thicker amounts of cushioning foam. Larger thicknesses of cushioning foam result in excess packaging sizes and concomitant elevated shipping costs.

It would be desirable to provide a closed cell cushioning foam adapted to provide improved cushioning properties at reduced static loadings.

In order to provide such an improved closed cell cushioning foam, the present inventors have investigated preparing strand foam or coalesced foam by the techniques disclosed in U.S. Patent 3,573,152. In particular, in using polyethylene resins and standard chlorofluoro- carbon blowing agents and a suitable die having a multitude of closely spaced small holes therein, the emerging strands could not be made to coalesce or adhere together under any processing conditions employed. In particular, when the foaming temperature of the resin was increased in an attempt to provide a tacky surface to the emerging strands, foam collapse was experienced. Similarly, when the strands were reheated after emerging from the die face, foam collapse was again experienced.

It has now been discovered that the ability of a foamable resin formulation to form a coalesced foam structure upon exiting a die containing a multiplicity of orifices and subsequently foaming is dependent on the existence of sufficient adhesion between neighbouring foam surfaces at the temperature required for such foaming. In particular, certain resins do not possess sufficient surface tacticity in the melt at the temperatures required for foaming to form the desired coalesced structure.

For various reasons high loadings of nucleating solids may also be incorporated into foam, particularly a large cross-section foam board. The nucleating additive may be, for example, a carbon black or a conductive fiber added to produce antistatic or conductive foam; a fire retardant added to improve foam fire resistance; an inert solid or fiber added to reduce processing costs or change the foam physical properties; an additional polymer added to change some foam property; a pigment added to change foam colour or appearance; or any other nucleating solid additive, semi-solid additive or combinations of such nucleating additives.

Often though, the amount of nucleating additives which can be added is severely limited due to the undesirable small cell size in the foam which results when the desired level of nucleating additives are added. This over nucleation results in small cross-

sections, folding of foam boards, excessive open cells, poor surface appearances and foam collapse. It is not possible sometimes to produce larger cross-section foams with the desired levels of the nucleating additives. Carbon black at a level of five (5) percent or greater and non-antimony fire retardants at a level of ten (10) percent are examples of these problems.

In order to provide such a highly loaded improved closed cell foam, the present inventors have investigated preparing highly loaded carbon black strand foam by the techniques disclosed in U.S. Patent 4,431,575. Although this patent reports a high loading of carbon black for polyolefin resin compositions, a stable polyethylene foam board through a single slot die with carbon black loadings above five (5) percent could not be obtained.

It would be desirable to provide a shaped strand foam comprising a thermoplastic resin.

It would be desirable to provide a shaped strand foam comprising an alkenyl aromatic resin, particularly a polystyrene resin or a polyolefin resin, particularly a polyethylene resin.

It would be desirable to provide a continuous method for producing a shaped strand foam comprising a thermoplastic resin.

It would be desirable to provide a continuous method for producing a shaped strand foam comprising an alkenyl aromatic resin, particularly a polystyrene resin or a polyolefin resin, particularly a polyethylene resin.

It would be desirable to provide a device for the continuous production of a shaped strand foam.

It would also be desirable to provide a homogeneous variable density closed cell shaped strand foam structure.

It would be desirable to provide a method for producing a strand foam comprising a polyolefin resin, particularly a polyethylene resin.

In addition, it would be desirable to provide a polyethylene resin strand foam suitable for cushioning objects having improved cushioning properties at low static loadings.

It would be desirable to provide a method for producing a highly loaded closed cell strand foam comprising an alkenyl aromatic thermoplastic synthetic resin particularly a polystyrene resin or a polyolefin resin, particularly a polyethylene resin.

In addition, it would be desirable to provide a highly closed cell polystyrene resin or polyethylene resin strand foam suitable for antistatic or electroconductive purpose.

Description of the Drawings

In Figure 1, there are depicted the cushioning properties of several closed cell polyolefin foams including a foam structure of the present invention. Further description of the preparation and testing of such foams is contained in Example 1.

In Figure 2, there is depicted a die face plate comprising narrow slits suitable for preparing a coalesced foam having a honeycomb structure.

In Figure 3, there is depicted a die face plate comprising small circular orifices suitable for preparing a coalesced foam.

In Figure 4, there is depicted a die face plate comprising small circular orifices, with some orifices closed, suitable for preparing a coalesced foam having an L-shaped structure.

In Figure 5, there is depicted a die face plate comprising small circular orifices, with some orifices closed, suitable for preparing a coalesced foam having a t-shaped structure.

In Figure 6, there is depicted a die face plate comprising small circular orifices, with some orifices closed, suitable for preparing a coalesced foam having internal voids.

In Figure 7, there is depicted a die face plate comprising small circular orifices, with some orifices closed, suitable for preparing a coalesced foam having a variable density.

Figures 8-10 are graphs showing the heat seal strength of various olefin resins and mixtures of resins and suitable foaming temperatures therefor.

Summary of the Invention

According to a first aspect of the present invention, there is provided a closed cell foam structure comprising a plurality of coalesced extruded strands or profiles of a foamed thermoplastic composition comprising, in polymerized form, at least one non-aromatic olefin having a heat seal strength at a foamable temperature of a film of the thermoplastic composition of at least 3.0 Newton/inch (2.5 cm) width and wherein the foam structure has a gross density from about 0.1 to about 5.0 lbs/ft^3 (0.2 - 8 kg/m^3) and the strands or profiles are disposed substantially parallel to the longitudinal axis of the foam.

According to a second aspect of the present invention, there is provided a closed cell foam structure comprising a plurality of coalesced extruded strands or profiles of a compatible mixture comprising: (a) an olefin polymer selected from the group consisting of homopolymers of ethylene or propylene, copolymers of ethylene or propylene and one or more C4-8 alpha-olefins, and mixtures thereof; and

(b) an interpolymer of ethylene and at least one comonomer, said interpolymer having a melting point less than the melting point of (a);

provided further that the foam structure has a density from about 0.5 to about 5.0 lbs/ft^3 (0.8 - 8 kg/m^3) and the strands or profiles are disposed substantially parallel to the longitudinal axis of the foam.

According to a third aspect of the present invention, there is provided a closed cell foam structure comprising a plurality of coalesced extruded foamed non-circular strands or profiles of thermoplastic material disposed in substantially parallel arrangement to the longitudinal axis of the foam characterised in that

adjacent strands or profiles are mutually orientated and/or shaped and are joined at their extremities to form, in cross-section of the structure, a network having voids of polygonal or closed curve

shape.

According to a fourth aspect of the present invention, there is provided a continuous method for producing a shaped closed cell foam structure comprising a plurality of coalesced extruded strands or profiles comprising:

(a) preparing a die by providing the die with a plurality of openings;

(b) blocking temporarily some of the openings so that the remaining openings form the desired shaped closed cell foam structure;

(c) attaching the die to an apparatus capable of preparing a foamable mixture;

(d) preparing the foamable mixture in the apparatus from a thermoplastic resin and a volatile blowing agent;

(e) forcing the foamable mixture through the die

(d) preparing the foamable mixture in the apparatus from a thermoplastic resin and a volatile blowing agent;

(e) forcing the foamable mixture through the die so that the foamable mixture foams at the die into the desired shaped closed cell foam structure.

The present invention provides also a die having a plurality of openings which may be temporarily blocked so as to provide a desired shaped closed cell foam structure comprising a plurality of coalesced extruded strands or profiles.

Also according to the present invention, there is provided a homogeneous variable density closed cell foam structure comprising a plurality of coalesced strands or profiles.

According to a fifth aspect of the present invention, there is provided a highly loaded closed cell foam structure comprising a plurality of coalesced extruded strands or profiles of a mixture comprising: (a) a thermoplastic resin selected from the group consisting of:

(1) an olefin resin blend of

(a) an olefin polymer selected from the group consisting of homopolymers of ethylene or propylene, copolymers of ethylene or propylene with one or more C4-8 alpha-olefins and mixtures thereof; and

(b) an interpolymer of ethylene and at least one comonomer, said interpolymer having a melting point less than the melting point of olefin polymer (a); and

(2) an alkenyl aromatic synthetic resinous material; and

(b) a nucleating additive in a range of about 0.5 to about 50 percent, based on the total weight of the thermoplastic resin;

provided further that the foam structure has a density from about 0.5 to about 5.0 lbs/ft^3 (0.8 - 8 kg/m^3) and the strands or profiles are disposed substantially parallel to the longitudinal axis of the foam.

Detailed Description of the Invention

The shaped strand foams of the present invention are prepared from a thermoplastic resin and a volatile blowing agent. In some aspects of the invention, the said resin is, depending upon the aspect, a non-aromatic olefin generally or a specified olefin polymer/interpolymer mixture. In other broader aspects, the resin is an alkenyl aromatic polymer or copolymer, particularly polymers and copolymers of styrene, or a olefin polymer or copolymer, particularly polyethylene.

The strand foams of the present invention are prepared by the extrusion foaming of a molten thermoplastic composition utilizing a die containing a multiplicity of orifices. The orifices are so arranged such that the contact between adjacent streams of the molten extrudate occurs during the foaming process and the contacting surfaces adhere to one another with sufficient adhesion to result in a unitary structure. Desirably, the individual strands or profiles of coalesced polyolefin foam should remain adhered into a unitary structure to prevent delamination under stresses encountered in preparing, shaping, and using the foam as a cushioning device.

As a technique for identifying suitable thermoplastic compositions for use in the present invention, the aforementioned measurement of heat seal strength of a film thereof is employed. "Heat seal strength" as used herein is defined as the adhesion generated between two film surfaces caused to adhere to one another by application of 40 lbs/in^2 (275 kPa) pressure for 1.0 sec. at the temperature being tested followed by cooling the film/film laminate for one minute. Such heat sealing may be performed by a SentinelR Hot Tack machine, Model 12ASL. Bond Strength (Heat Seal Strength) is the force in Newtons/inch (2.5 cm) width required to cause tearing of at least 50% of the seal area by 180° pull testing. The test constitutes a modification of Dow heat seal test FS-222 and ASTM F-88. Films of the various materials to be tested may be prepared by placing pellets of the appropriate resin between polyethylene terephthalate sheets placed in a 10" x 2" (25 x 5 cm) press heated to 180°C. After one minute preheating, the pellets are compressed under a pressure of 5,000 lbs/in^2 (35 MPa) for three minutes, cooled, and cut into 1" x 10" strips. Film thickness from .004 to .006 inch (0.10 -0.15mm) result.

The heat seal strength of a thermoplastic composition is dependent on the temperature thereof, and generally rises as temperature is increased. However, suitable foams may be prepared only in a narrow temperature range. This temperature range is uniquely defined for each foamable composition and is dependent on several factors, most importantly the melt strength of the foamable thermoplastic composition at the temperature range of interest. This in turn is subject to several factors such as the particular thermoplastic resin used, the amount and type of blowing agent employed, amount and types of fillers, nucleating agents and additional additives, the presence or absence of crosslinkers, etc. Accordingly, depending on the density of the individual strands of foam utilized in the present invention (referred to as strand density or local density), the extrusion temperature that must be employed is severely limited to generally only about 2°C temperature range. In order to satisfy the

requirements of the present invention, the resin should possess at least the aforementioned heat seal strength at such temperature.

In the appended drawings, Figures 8-10 illustrate the above requirements. For various representative thermoplastic resins or blends actual heat seal strengths are provided. Also illustrated are approximate foaming temperatures for such resins. A resin may suitably be employed according to the present invention only if adequate surface adhesion between adjacent strands is generated under the conditions required for producing a foam. It is seen that such condition may be accurately predicted by reference to a film seal strength measurement of the same thermoplastic composition at the temperatures in question such as are provided in Figures 8-10.

As suitable thermoplastic resins comprising, in polymerized form, a non-aromatic olefin there may be utilized copolymers of ethylene and a copolymerizable polar monomer especially a carboxyl-containing comonomer. Examples include copolymers of ethylene and acrylic acid or methacrylic acid and C_{1-4} alkyl ester or ionomeric derivatives thereof; ethylene vinylacetate copolymers; ethylene/carbon monoxide copolymers; anhydride containing olefin copolymers of a diene and a polymerizable copolymer; copolymers of ethylene and an alpha-olefin having ultra low molecular weight (i.e. densities less than 0.92); blends of all of the foregoing resins; blends thereof with polyethylene (high, intermediate or low density); etc. Particularly preferred theremoplastic compositions are random, homogeneous, copolymers of ethylene and acrylic acid, (EAA copolymers) having up to about 10% by weight of copolymerized acrylic acid; ionomeric derivatives of the foregoing, copolymers of ethylene and vinyl acetate; ultra low density polyethylene; and blends of the foregoing with one another and with low density polyethylene.

In the second aspect of the invention, the polyethylene strand foams are prepared from a homogeneous blend of olefin resins. Component (a) of the resin blend may be any homopolymer of ethylene, e.g., low density polyethylene; high density polyethylene; intermediate density polyethylene; or ultra-high molecular weight polyethylene, a copolymer of ethylene and one or more C_{4-8} alpha-olefins, e.g., linear low density polyethylene, or a mixture thereof. Preferably, component (a) comprises low density polyethylene having a density from about 0.90 to 0.95 g/cm³ and the melt flow rate from about 0.1 to 10. Most preferably, the melting point of component (a) is from about 100 to about 130°C.

Preferred amounts of component (a) in the resin blend are from about 60 percent to about 90 percent by weight.

Component (b) comprises an interpolymer of ethylene and at least one additional comonomer. Examples of suitable comonomers include the well known carboxyl-containing ethylenically unsaturated comonomers having up to about 12 carbons, especially ethylenically unsaturated carboxylic acids and ethylenically unsaturated carboxylic acid esters, ethylenically unsaturated dicarboxylic acid anhy-

drides, etc. Additional suitable comonomers include carbon monoxide, conjugated dienes such as butadiene, etc. Preferred comonomers are carboxyl-containing ethylenically unsaturated comonomers. Highly preferred comonomers include ethylenically unsaturated C_{3-8} carboxylic acids such as acrylic acid, methacrylic acid, etc. and C_{1-5} alkyl esters thereof; vinyl esters such as vinyl acetate; and ethylenically unsaturated dicarboxylic acid anhydrides such as maleic anhydride.

The polymers of ethylene and at least one carboxyl-containing comonomer may be prepared by addition polymerization according to known techniques, or by a grafting reaction of the reactive carboxyl-containing comonomer with a preformed polymer of ethylene. Additional elastomeric components such as polyisobutylene, polybutadiene, ethylene/propylene copolymers, and ethylene/propylene/diene interpolymers may be included in the blend if desired but are not preferred. Moreover, additional components such as crosslinking agents designed either to provide latent crosslinking of the ethylenic polymer, such as the silane functional crosslinking agents or covalent or ionic crosslinking agents, may be included if desired. Mowever, in the nucleating agent-aspect of the present invention, for large cross-section ethylenic polymer foam board it is preferred that the foam be non-crosslinked.

In a preferred resin composition, component (b) comprises a copolymer of ethylene and acrylic acid or ethylene and vinyl acetate containing from about 85 percent to about 98 percent ethylene. Most preferably, component (b) is a homogeneous random copolymer of ethylene and acrylic acid. Random homogeneous copolymers of ethylene and acrylic acid may be obtained under the tradename EAA available from The Dow Chemical Company. Ethylene vinyl acetate copolymers may be obtained under the tradename Elvax from E.I. duPont deNemours & Company. Anhydride modified copolymers of ethylene are available under the tradename Plexar from Norchem, Inc. Ionomeric copolymers are available under the tradename Surlyn® from E.I. dufont de Namours & Co.

In yet another preferred resin composition, component (b) comprises an ionomer which is an ethylene copolymer with pendant carboxylic acid groups partially or completely neutralized with cations such as NH^{4+}, Na^+, Zn^{++}, and Mg^{++}, Such ionomers may be obtained under the tradename Surlyn from E.I. duPont de Nemours & Co.

By the term "compatible" is meant that components (a) and (b), when mixed, demonstrate either a single Tg or distinct Tg's such that the differences between them is less than the differences between the separately measured Tg's of the unblended components.

Blending of component (a) and component (b) in order to provide a suitable resin for melt extrusion to prepare the strand foams of the present invention is accomplished according to known techniques in the art. Suitably, a mixer, extruder or other suitable blending device is employed to obtain a homogeneous melt. An extruder or any other suitable device is then employed to incorporate a known blowing

agent such as a chlorofluorocarbon, e.g., 1,2-di-chloro-tetrafluoroethane, 1,2-difluorotetrachlo-roethane, chlorotrifluoromethane, and mixtures thereof with additional agents such as halogeneted hydrocarbons, hydrocarbons, carbon dioxide, water, etc. Additional agents such as nucleating agents, extrusion aids, antioxidants, colorants, pigments, etc., may also be included in the blend.

Provided that the resin meets the heat seal strength requirement of the first aspect of the invention, resin (a) or resin (b) as specified above can be used alone instead of in the specified mixture of (a) and (b).

Alternatively an alkenyl aromatic thermoplastic synthetic resin may be selected to produce the strand foam. By the term "alkenyl aromatic thermo-plastic synthetic resin is meant a solid polymer of one or more polymerizable alkenyl aromatic compounds. The polymer or copolymer comprises in chemically combined form, at least 50 percent by weight of at least one alkenyl aromatic compound having the general formula

$$Ar - \underset{\underset{R}{|}}{C} = CH_3$$
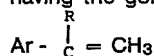
wherein Ar represents an aromatic hydrocarbon radical, or an aromatic halo-hydrocarbon radical of the benzene series, and R is hydrogen or the methyl radical. Examples of such alkenyl aromatic resins are the solid homo polymers of styrene, alpha-methyl-styrene, o-methylstyrene, m-methylstyrene, p-me-thylstyrene, ar-ethylstyrene, ar-vinylxylene, ar-chlo-rostyrene, ar-bromostyrene; the solid copolymers of two or more of such alkenyl aromatic compounds with minor amounts of other readily polymerizable olefinic compounds such as methylmethacrylate, acrylonitrile, maleic anhydride, citraconic anhydride, itaconic anhydride, rubber reinforced (either natural or synthetic) styrene polymers, etc.

The volatile blowing agents are those convention-ally known for alkenyl aromatic thermoplastic resin foams.

Additional agents such as nucleating agents, extrusion aids, antioxidants, colorants, pigments, etc. may also be included in the alkenyl aromatic thermoplastic resin or the olefin resin blend. How-ever, those that function as nucleating additives, which cause foam problems can now be added in an amount of from about 0.5 to about 50 weight percent, based on resin weight, into the foams of the present invention. Those preferred highly loaded closed cell coalesced foam structures are those having a large cross-section.

Large cross-section foam and board foams are terms which define those foam structures having a cross-section area of at least twelve (12) square inches (80 cm²), preferably at least 18 square inches (120 cm²), and a minimal cross-sectional dimension of at least one quarter inch (6 mm), preferably one half inch (13 mm).

The molten extrudate is then forced through a die plate comprising numerous small holes in a suitably desired spacial arrangement or alternatively an array of slits, desirably in an oscillating form such as a sine wave, honeycomb, square saw tooth or triangular saw tooth wave pattern. Most desirably, the alternat-ing slits are offset so that maxima and minima of adjacent rows are aligned with one another so as to assure contact between rows of extrudate. In the preferred embodiment of the invention, illustrated in Figure 2, the die face plate, 1, contains several rows of narrow slits, 2, comprising equal length segments joined at 60° angles and aligned with respect to neighbouring slits to provide a honeycomb shaped foam structure of separately extruded and coa-lesced profiles. Such foams prepared wherein the adjoining profiles contain sections adjacent one another having significant surface areas in mutual contact are particularly desired in order to provide structures of improved strength.

Alternatively in the use of holes in the die face plate, various geometric shapes particularly non-cir-cular shapes, such as X-, cross-or star-shaped geometry may be employed. The holes or slits may be generated in the die face plate by the use of electromagnetic discharge or laser cutting technol-ogy as is well-known in the art. The spacing and arrangement of the holes or slits in the die face plate may be adjusted in order to vary the ultimate cushioning properties of the strand foam and provide in cross-sectional view, coalesced foam structures of repeating structure containing voids having the shape of polygons or closed curves of any description. The only limitation on spacial arrangement of the die orifices is that contact and coalescence of adjacent strands or profiles after extrusion from the die face plate must be achieved.

In a preferred embodiment of the invention, illustrated in Figure 3, the die face plate, 1, contains several rows of small circular holes, 2, which rows may be aligned so that the holes in each row are directly over each other or are offset, as seen in Figure 3. The holes may vary in size, but preferably the holes are the same size and preferably that size is about 0.1 inch (2.5 mm) diameter or less. Preferably the hole size is less than about 0.05 inch (1.3 mm) diameter.

The present invention, with hole sizes less than about 0.1 inch (2.5 mm) in diameter, cause a high pressure drop which acts to very uniformly distribute the flow through each hole even if the die face is larger than the diameter of the foamable material stream entering the die. This eliminates the need to make compensations for flow distribution in a specific die design, thus allowing the making of complicated shapes without concern for a flow distribution effect.

By providing a single die with a large number of small holes, as opposed to a specially produced die useful in producing only a single shape, a variety of complicated shapes can be produced from the same die by sealing or blocking all the holes but the holes of the desired shape.

The sealing or blocking of holes can be one by any method, such as for example remote actuation of hole blockers, but the preferred methods are the sealing of the holes with a material which can be removed, such as epoxy, or the placing of a template on the side of the die that first receives the flow of foamable material so that the template effectively seals off the holes that are desired to be blocked.

The sealing material or template is easily removable so that another shape can be quickly produced from the same die with a different template or configuration of sealing material with minimal amount of time necessary to change the die.

Figures 4, 5 and 6 illustrate the die face plate, 1, having the small circular holes, 2, of Figure 3 with some sealed or blocked holes, 3. These dies can then continuously produce the shapes shown.

It is also possible, according to the present invention, to produce multiple shapes from a single die.

Foams having gross densities (that is bulk densities or densities of the closed-cell foam including interstitial volumes between strands or profiles) varying from about 0.2 to about 5 pounds per cubic foot (0.3 - 8 kg/m³) may be obtained according to the foregoing technique. Preferred foams are those having a density from about 0.5 to about 3.0 lb/ft³ (0.8 - 4.8 kg/m³), especially from about 1.0 to about 2.8 pounds per cubic foot (1.6 - 4.5 kg/m³) and most preferably from about 1.2 to about 2.0 pounds per cubic foot (1.9 - 3.2 kg/m³). The individual strands of foam preferably have a local or strand density from about 0.5 to about 6 lbs/ft³ (0.8 - 9.6 kg/m³) and most preferably from about 1.0 to 3.0 lbs/ft³ (1.6 -4.8 kg/m³).

The open channels or voids in the foams of the present invention are arranged in a direction parallel to the extruded strands. The presence of such open channels contributes to the unique cushioning properties of the present invented foam and their shape, size, and frequency of occurrence may be varied through adjustments of the size, location and shape of the die face plate's holes or slits. In one embodiment, the voids occurring in the interior of the foam structure or in one portion thereof may be larger, differently shaped or more or less numerous than those voids that are nearer the surface or in the remaining portion of the foam structure in order to provide tailored cushioning properties in the resulting structure. Preferably the individual strands have a maximum cross-sectional dimension and the profiles have a maximum thickness from about 0.5 to about 10.0 mm, most preferable 1.0 to 5.0 mm.

The coalesced strands may form a board or other object having a larger cross-sectional area than is possible utilizing existing polyolefin foam extrusion techniques. For example, utilizing equivalent extrusion rates, a foam structure according to the invention may be prepared having a cross-section that is up to 8 times larger than the maximum cross-sectional area of an extruded foam article prepared utilizing a single orifice opening.

Desirably, foams according to the present invention allow the achievement of improved cushioning of objects particularly at low static loadings. For example, preferably according to the present invention, two inch (5 cm) thick samples of the invented closed-cell strand foams when tested at a 24 inch (61 cm) drop height have dynamic cushioning properties such that objects inducing static loads (SL) of from about 0.18 to about 0.5 lb/in² (1.2 - 3.4 kPa) at the earth's surface experience a peak deceleration of less than about 65 G's (640 m/s²),

preferably loads of from about 0.15 to about 0.4 lb/in² (1.0 - 2.8 kPa) experience peak decelerations of less than about 55 G's (540 m/s²). In measuring such cushioning properties, the technique employed is ASTM D-1596.

Having described the invention, the following examples are included as illustrative and are not to be construed as limiting. Parts per hundred measurements are based on the resin weight.

Example 1

A blend of 80 weight percent polyethylene (PE-620, available from The Dow Chemical Company) and 20 weight percent of a homogeneous random copolymer of ethylene and acrylic acid containing approximately 6.5 percent acrylic acid (EAA-459 available from The Dow Chemical Company) and 22 parts per hundred 1,2-dichlorotetrafluoroethane blowing agent is extruded through a 1.5 inch (3.8 cm) extruder connected to a die having 89 equally spaced circular shaped holes arranged in five rows. The holes were approximately 0.040 inches (1.0 mm) in diameter and spaced approximately 0.125 inches (3.2 mm) between centres. Upon extrusion, the individual strands adhered to one another to form a uniformly coalesced closed-cell structure. No evidence of foam instability was observed. The resulting foam had a gross density of about 2.4 pounds per cubic foot (3.8 kg/m³) and had approximately 10 percent by volume open channels running in parallel rows in the extrusion direction. The diameter of the closed-cell strands was approximately 0.125 inch (3.2 mm).

Example 2

The conditions of Example 1 were substantially repeated excepting that the resin blend comprised approximately 40 percent by weight of a homogeneous random copolymer of ethylene and acrylic acid containing 6.5 percent acrylic acid (EAA-459 available from The Dow Chemical Company) and 30 parts per hundred 1,2-dichlorotetrafluoroethane blowing agent. The remainder of the resin blend comprised low density polyethylene (PE-620 available from The Dow Chemical Company). The resin blend was extruded through a die face plate having approximately 800 holes. Each hole was approximately 0.04 inches (1.0 mm) in diameter. Holes and rows were equally spaced at approximately 0.125 inches (3.2 mm) between centres. The resulting foam had approximately 15 percent open volume in channels running in the extrusion direction and had a foam density of 1.8 pounds per cubic foot (2.9 kg/m³).

Example 3

A die face plate having 28 individual X-shaped incisions with the height and width of each X being approximately 0.10 inches (2.5 mm) and the width of the incision being approximately 0.015 inches (0.4 mm). The X-shaped incisions were arranged in 5 rows, spaced approximately .0625 inches (1.6 mm) apart. A resin blend substantially the same of that in Example 1 was then extruded through the die face plate at a rate such that, upon expansion, the resulting X-shaped foam strands contacted one

another on the tips only of the X-shaped cross-sectional dimensions. The resulting foam contained approximately 35 percent by volume open channels in the extrusion direction of the plank. The foam gross density was 2.6 pounds per cubic foot (4.1 kg/m³).

Example 4

A die face plate having 2600 holes holes 0.040 inches (1.0 mm) in diameter and 0.1 inch (2.5 mm) long is arranged in a rectangular pattern 1.70 inches (43.2 mm) by 21.0 (533.4 mm) inches with a 0.12 inch (3.0 mm) spacing between holes. A blend of 80 weight percent polyethylene (PE-620, available from The Dow Chemical Company) and 20 weight percent of a copolymer of ethylene and acrylic acid containing approximately 9.0 percent acrylic acid (EAA-459 available from The Dow Chemical Company), 28 parts per hundred 1,2-dichlorotetrafluoroethane blowing agent and 0.5 parts per hundred talc is extruded, mixed, cooled to 110 °C and forced through the die face plate. Various shapes, including a plank measuring 26 inches (660 mm) wide by 2.37 inches (60 mm) thick, are produced. The plank has excellent strand adhesion and the thickness of the plank varies no more than two (2) percent of the total thickness. The standard deviation of sixty measurements across the width vary only +/- 0.8 percent. This precise thickness measurement is important because it is accomplished without the aid of a post-extrusion forming method. Most complicated shaped strand foams would also be produced without the aid of a post-extrusion forming method.

Example 5

A blend of 80 weight percent polyethylene (PE-620, available from The Dow Chemical Company) and 20 weight percent of Suryln-8660 (obtained from E.I. duPont de Nemours & Co.), 26 parts per hundred of a mixture of 1,2-dichlorotetrafluoroethane and dichlorodifluoromethane blowing agent and 0.8 parts per hundred talc is extruded, mixed, cooled and forced through the die face plate of Example 4. Nine hundred (900) holes in the die are blocked off to provide a homogeneous variable density closed cell strand foam plank having the following characteristics: at about 16 percent through the thickness direction from the top of the structure the density is about 2.02 lb/ft³ (3.23 kg/m³); at about 33 percent from the top of the structure the density is about 2.18 lb/ft³ (3.49 kg/m³); at about 50 percent from the top of the structure the density is about 2.54 lb/ft³ (4.06 kg/m³); at about 67 percent from the top of the structure the density is about 2.79 lb/ft³ (4.46 kg/m³); and at about 77 percent fron the top of the structure the density is about 2.45 lb/ft³ (3.92 kg/m³). This shows that variable density closed cell strand foam structures are easily and quickly produced.

Figure 7 illustrates a die configuration for a homogeneous variable density closed cell strand foam structure with the die face plate, 1, having openings, 2, and a first level of blocked openings in multiples of three, 3, a second level of blocked openings in multiples of two, 4, a third level of single blocked openings, 5, and a last level having no blocked openings.

Example 6

A blend of 80 weight percent polyethylene (PE-4005, available from The Dow Chemical Company) and 20 weight percent of Suryln-8660 (obtained from E.I. duPont de Nemours & Co.), and 23 parts per hundred 1,2-dichlorotetrafluoroethane blowing agent is extruded through a 1.5 inch (38.1 mm) extruder connected to a die having 89 equally spaced circular shaped holes arranged in five rows. The holes were approximately 0.040 inches (1.0 mm) in diameter and spaced approximately 0.125 inches (3.2 mm) between centres. Levels of 5, 7.5, 8.5 and 10 weight percent carbon black (Ketjenblack 600, a product of AKZO Chemie N.V.) are added. The resulting foams are stable with a surface appearance and size equivalent to strand foams containing no carbon black. The foam densities range from about 3.0 to about 3.5 lb/ft³ (4.8 to 5.6 kg/m³) and have a volume resistivity in the range of about 105 to about 109 ohms/centimeter.

Testing

Various conventional polyolefin resin foams and the strand foam of Example 2 were tested for cushioning properties. Two inch (5 cm) thick samples of closed cell foams were tested for peak deceleration at 24 inch (61 cm) drop heights. Eesides a foam according to the invention prepared according to Example 2, three additional conventional closed-cell foams (a, b, c) were tested. a) was a foam of 1.4 lbs/ft³ (2.2 kg/m³) density comprising a blend of ethylene acrylic acid and ethylene vinyl acetate (25 weight percent EAA-1430 available from The Dow Chemical Company, and 75 percent Elvax 470, available from E.I. duPont deNemours & Company). b) and c) were conventional closed-cell polyethylene foams of 1.8 and 2.4 pounds per cubic foot (2.9 and 3.8 kg/m³) density, respectively. Cushioning properties were measured according to ASTM D-1596. The results are contained in Figure 1. In the figure, Example 2, is the result obtained for the foam of Example 2, and (a), (b) and (C) identify the results obtained for foams (a), (b) and (c), respectively. A computer generated empirical fit is supplied for each of the foams. The fit is a formula, wherein peak deceleration, measured in G's, is defined as a function of static load (SL) for the various curves.

By reference to Figure 1 and the results of the testing, it may be seen that a unique cushioning ability at reduced static loadings is obtained by the foams according to the present invention. In particular, at static loads from about 0.1 to about 0.5 pounds per square inch (0.7 to 3.5 kPa), the strand foams of the present invention produce peak decelerations from about 65 to about 45 G's (640 to 440 m/s²) or less. More particularly, at static loadings from about 0.15 to about 0.4 lbs/in² (1.0 to 2.8 kPa), the compositions of the invention provide peak decelerations less than about 55 G's (540 m/s²) , which are unattainable by the use of equivalent thicknesses of conventional foam

cushioning materials.

The computer generated fit for the various curves are as follows:

Example 2 G's = 20.7 + 31.1(SL) + 4.3/SL

a   G's = 32.5 + 38.2(SL) + 2.5/SL

b   G's = 3.2 + 37.2(SL) + 10.9/SL

c   G's = 7.2 + 30.1(SL) + 17.7/SL

Accordingly, foams according to the invention are capable of providing peak decelerations measured in G's in the range of static loadings from about 0.15 to about 0.4 lb/in² (1.0 to 2.8 kPa) less than or equal to the value determined by the formula G's = 2.07 + 31.1(SL) + 4.3/SL.

While cushioning properties are necessary for some foam uses, other uses may require only high loading of a nucleating additive, while still others may require both.

Claims

1. A closed cell foam structure comprising a plurality of coalesced extruded strands or profiles of a foamed thermpolastic composition comprising, in polymerized form, at least one non-aromatic olefin having a heat seal strength at a foamable temperature of a film of the thermoplastic composition of at least 3.0 Newton/ inch (2.5 cm) width and wherein the foam structure has a gross density from about 0.1 to about 5.0 lbs/ft³ (0.2 - 8 kg/m³) and the strands or profiles are disposed substantially parallel to the longitudinal axis of the foam.

2. A foam as claimed in Claim 1, wherein a 5 cm (2 in) thick sample has dynamic cushioning properties such that objects inducing static loads of from 1.0 to 2.8 kPa (0.15 to 0.4 lbs/in²) dropped from a height of 61 cm (24 inches) at the earth's surface experience a peak deceleration of less than 540 m/s² (55 G's).

3. A closed cell foam structure comprising a plurality of coalesced extruded strands or profiles of a compatible mixture comprising:

(a) an olefin polymer selected from homopolymers of ethylene or propylene, copolymers of ethylene or propylene with one or more C₄₋₈ alpha-olefins and mixtures thereof; and

(b) an interpolymer of ethylene and at least one comonomer, said interpolymer having a melting point less than the melting point of olefin polymer (a); provided further that the foam structure has a density from 0.8 to 8 kg/m³ (0.5 to 5.0 lbs/ft³) and the strands or profiles are disposed in substantially parallel arrangement to the longitudinal axis of the foam.

4. A closed cell foam structure comprising a plurality of coalesced extruded foamed non-circular strands or profiles of thermoplastic material disposed in substantially parallel arrangement to the longitudinal axis of the foam characterised in that adjacent strands or profiles are mutually

orientated and/or shaped and are joined at their extremities to form, in cross-section of the structure, a network having voids of polygonal or closed curve shape.

5. A foam as claimed in Claim 4, wherein the strands or profiles are mutually orientated to maximize the void volumes.

6. A foam as claimed in Claim 4 or Claim 5, wherein the structure comprises strands of angular or concave cross-sections.

7. A foam as claimed in Claim 6, wherein the strands have a plurality of arms or teeth radiating from their longitudinal axis.

8. A foam as claimed in Claim 4 or Claim 5, wherein the structure comprises profiles of oscillatory form with the maxima and minima of adjacent profiles aligned.

9. A homogeneous variable density closed cell foam structure comprising a plurality of coalesced extruded strands or profiles with the strands or profiles when coalesced describing in cross-section a repeating structure containing voids and further provided that the foam structure has a variable density along a thickness or width axis with the range of the density being 0.8 to 8 kg/m³ (0.5 to 5.0 lbs/ft³) and the strands or profiles disposed in substantially parallel arrangement to the longitudinal axis of the foam.

10. A highly loaded closed cell foam structure comprising a plurality of coalesced extruded strands or profiles of a mixture comprising:

(a) a thermoplastic resin selected from:

(1) an olefin resin blend of

(a) an olefin polymer selected from homopolymers of ethylene or propylene, copolymers of ethylene or propylene with one or more C4-8 alpha-olefins and mixtures thereof; and

(b) an interpolymer of ethylene and at least one comonomer, said interpolymer having a melting point less than the melting point of olefin polymer (a); and

(2) an alkenyl aromatic synthetic resinous material; and

(b) a nucleating additive in a range of about 0.5 to about 50 percent, based on the total weight of the thermoplastic resin;

provided further that the foam structure has a density from 0.8 to 8 kg/m³ (0.5 to 5.0 lbs/ft³) and the strands or profiles are disposed in substantially parallel arrangement to the longitudinal axis of the foam.

11. A foam as claimed in Claim 10 or Claim 11, wherein the nucleating additive is carbon black present in a range of 5 to 50 percent.

12. A foam as claimed in any one of Claims 1, 2 and 4 to 11, wherein the thermoplastic resin is selected from random, homogeneous, copolymers of ethylene and acrylic acid having up to 10 percent acrylic acid and ionomeric derivatives thereof; ethylene-vinyl acetate copolymers; ultra low density polyethylene; blends thereof and blends thereof with low density polyethylene.

13. A foam as claimed in any one of Claims 1, 2

and 4 to 11, wherein the thermoplastic resin is: an olefin resin blend of

>   (a) an olefin polymer selected from homopolymers of ethylene or propylene, copolymers of ethylene or propylene with one or more C_{4-8} alpha-olefins and mixtures thereof; and
>
>   (b) an interpolymer of ethylene and at least one comonomer, said interpolymer having a melting point less than the melting point of olefin polymer (a).

14. A foam as claimed in any one of Claims 1, 2 and 4 to 11, wherein the thermoplastic resin is an alkenyl aromatic synthetic resinous material.

15. A foam as claimed in Claim 14, wherein the alkenyl aromatic synthetic resinous material is polystyrene.

16. A foam as claimed in any one of the preceding claims, wherein the strands are each 0.5 to 10.0 mm in the largest cross-sectional dimension, or the profiles are each 0.5 to 10.0 mm in cross-sectional thickness.

17. A foam as claimed in any one of the preceding claims, wherein the strands have a non-circular cross-sectional shape.

18. A foam as claimed in Claim 17, wherein the strand's cross-sectional shape is that of a star, cross or X.

19. A foam as claimed in any one of the preceding claims, wherein the strands or profiles when coalesced describe in cross-section a repeating structure containing voids having the shape of polygons or closed curves.

20. A method of preparing a foam structure as claimed in any one of Claims 1, 3, 4, 9 and 10, comprising extruding the foamable molten thermoplastic composition through a die plate having a plurality of orifices or an array of slits arranged so that adjacent strands or profiles extruded therethrough contact and coalesce to form a foam structure in which said strands or profiles are disposed substantially parallel to the longitudinal axis of the foam.

21. A method for continuously producing a shaped closed cell foam structure comprising a plurality of coalesced extruded strands or profiles comprising:

>   (a) providing a die with a plurality of openings;
>
>   (b) blocking temporarily some of the openings so that the remaining openings form a desired shaped closed cell foam structure;
>
>   (c) preparing the foamable mixture from a thermoplastic resin and a volatile blowing agent;
>
>   (d) forcing the foamable mixture through the die so that the foamable mixture foams at the die into the desired shaped closed cell foam structure.

22. A method as claimed in Claim 21, wherein the die has at least one hundred circular openings having a diameter of less than 2.5 mm (0.1 inches).
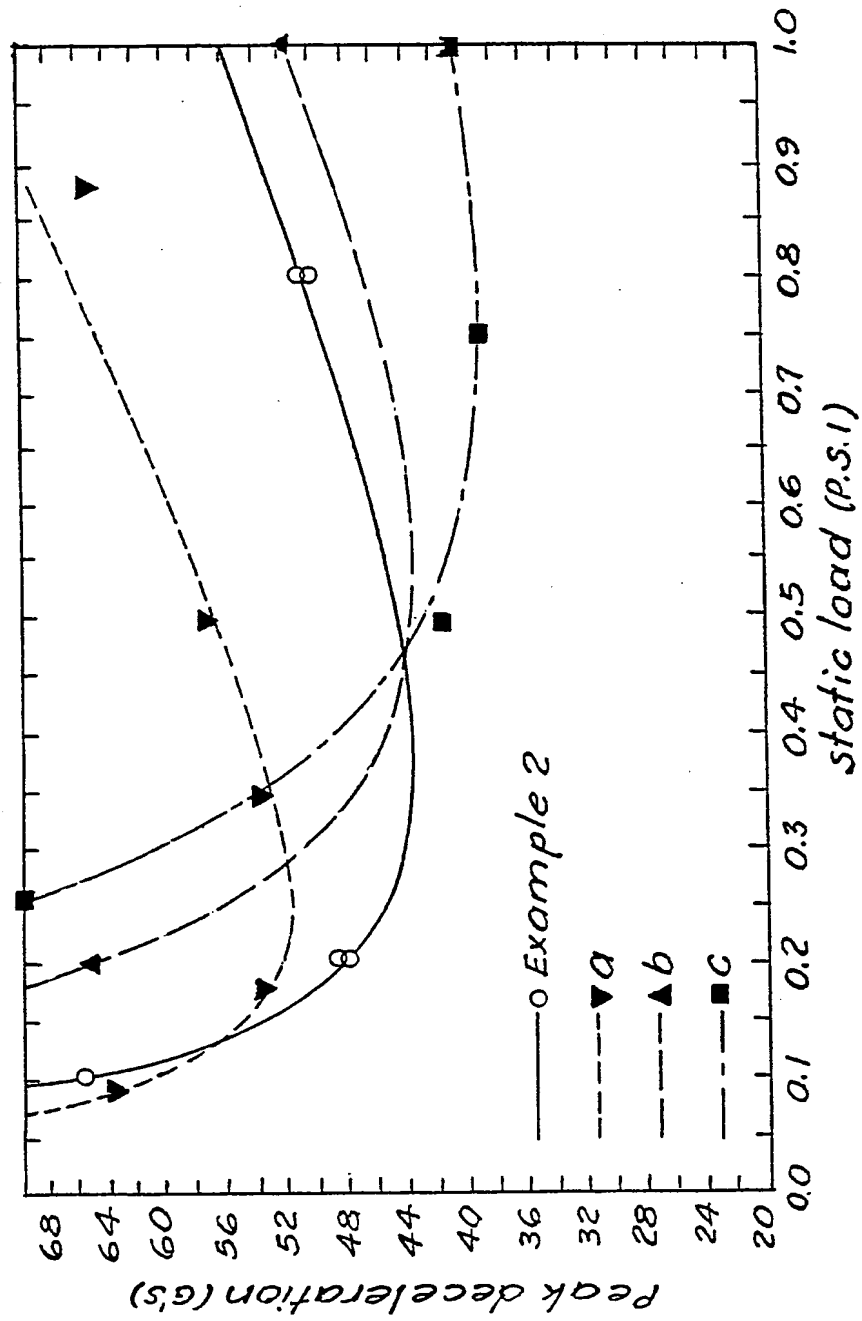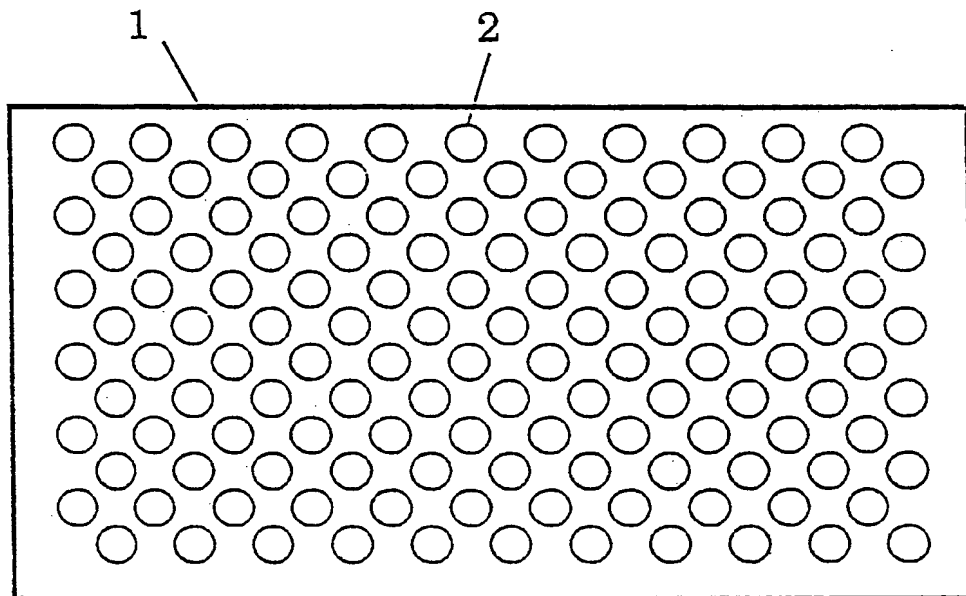
5

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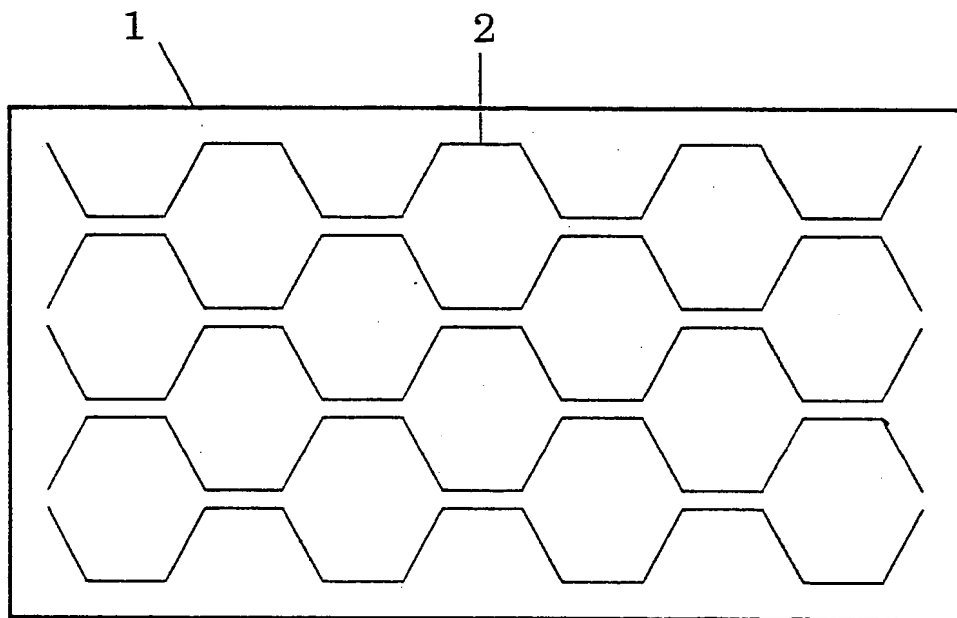
65

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FIG.1

Axis labels: static load (P.S.I) ; Peak deceleration (g's)

Legend: o Example 2 ; ▼ a ; ◄ b ; ■ c

FIG.2

FIG.3
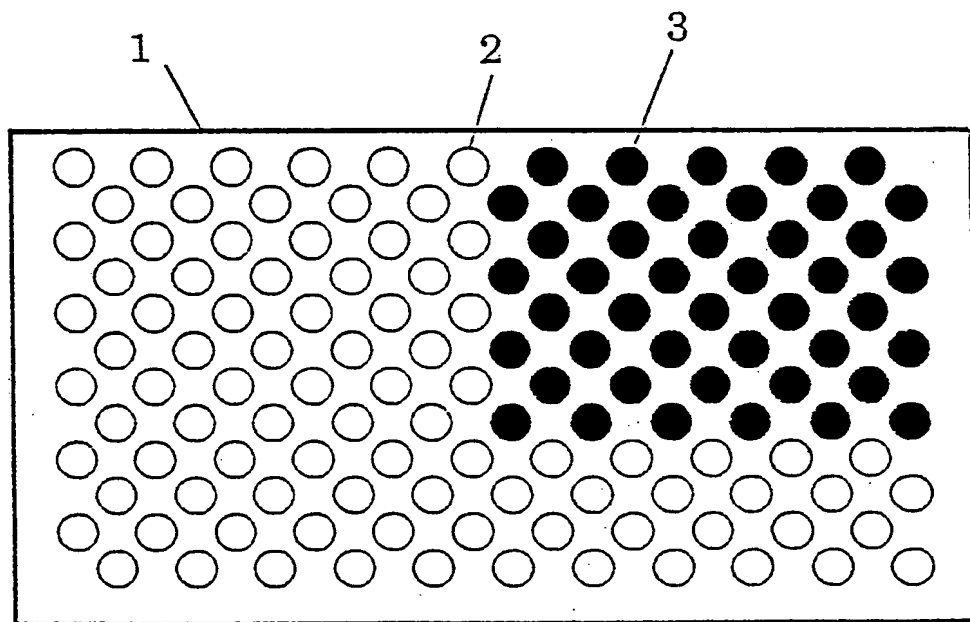
FIG.4
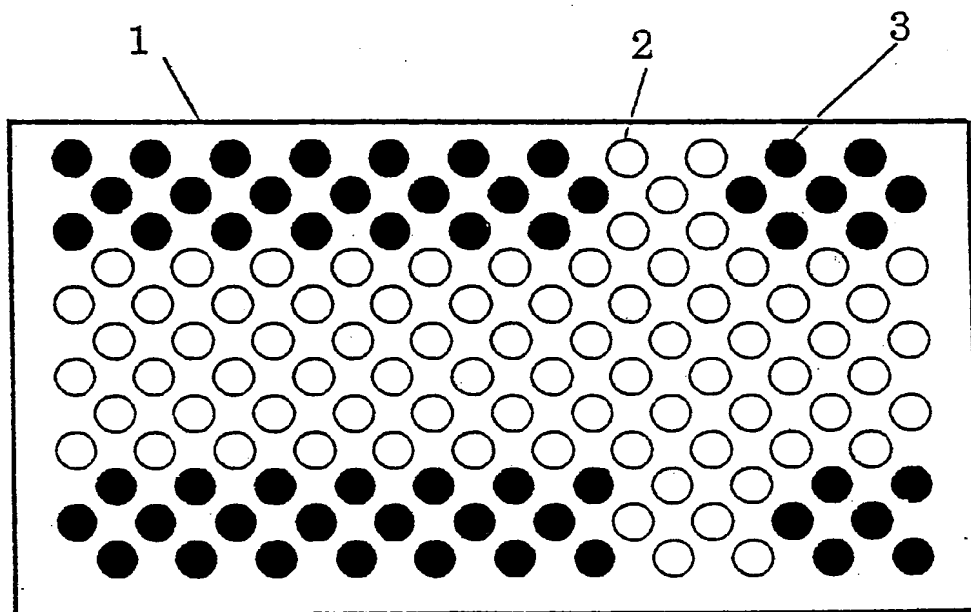
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FIG.5
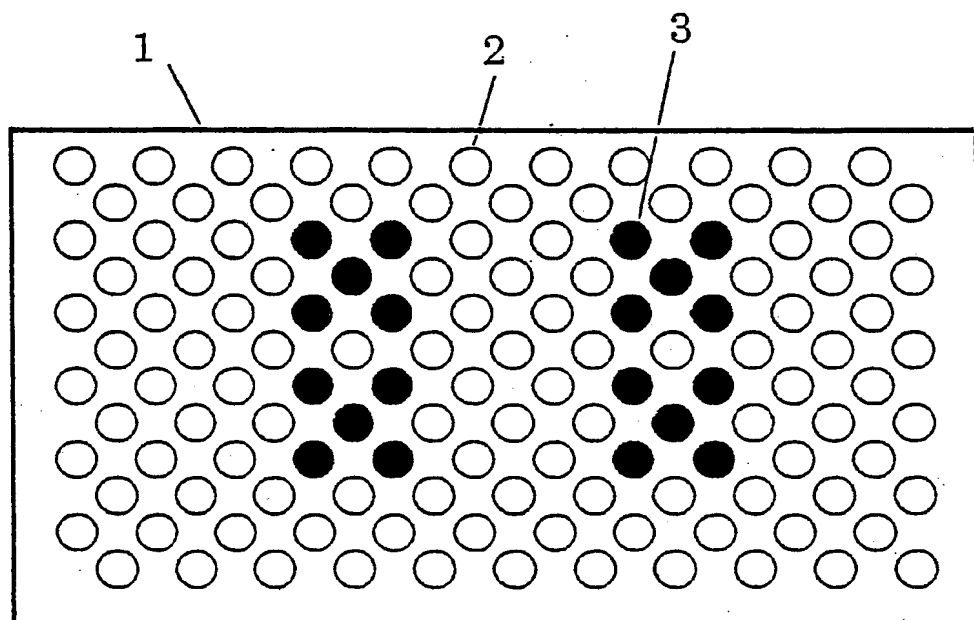
FIG.6
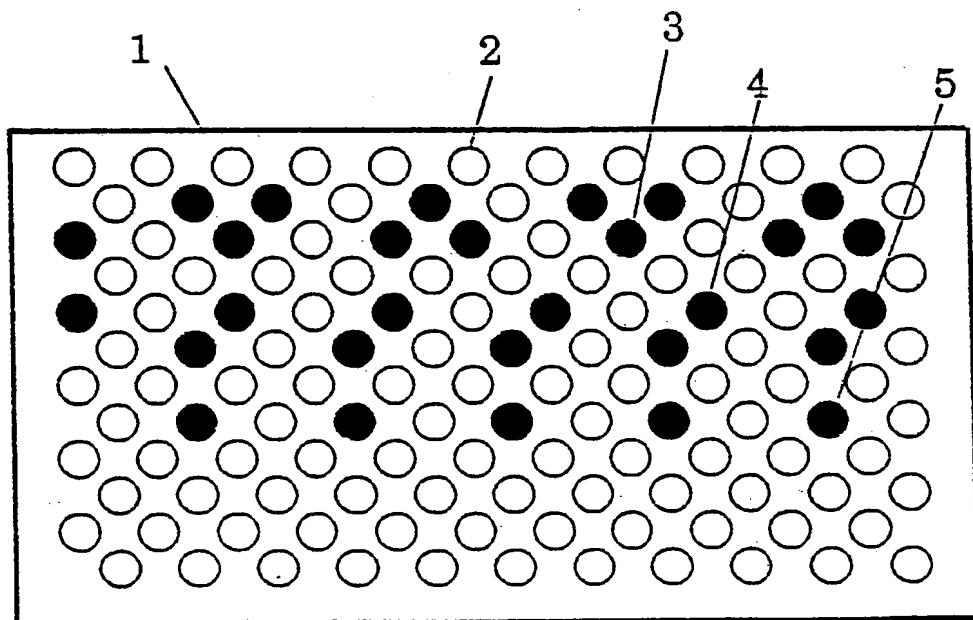
FIG.7

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Heat Seal Strength
(Newtons/ inch width)

FIG.8

Excellent
Adhesion

Good
Adhesion

Sealing
Temp.
°C.

94   96   98   100   102   104   106   108   110   112   114
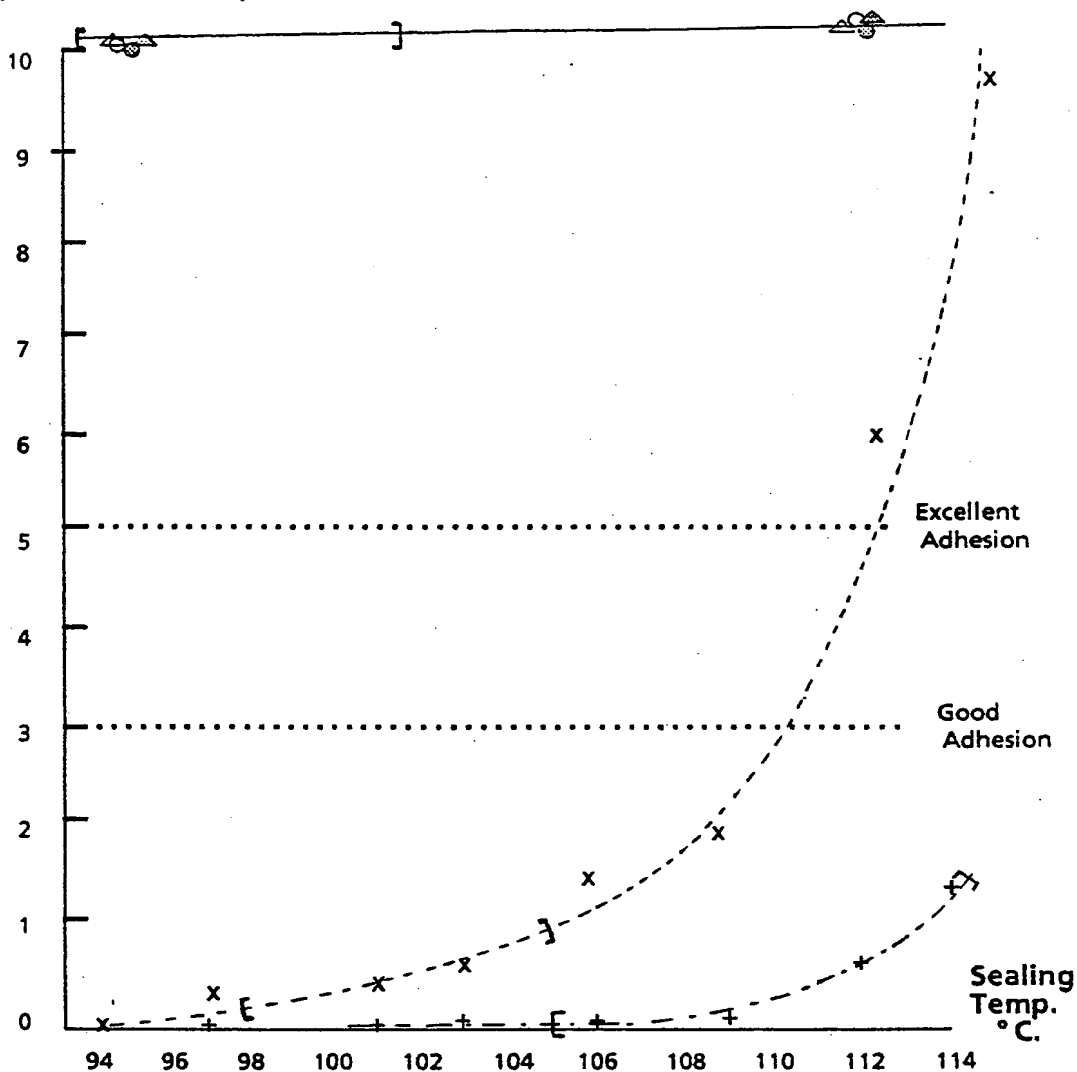
○ EAA-1420, ethylene/acrylic acid copolymer   _____

● EVA-1521, ethylene/vinyl acetate copolymer   _____

△ PE-4003 ultra low density polyethylene   _____

▲ Surlyn™ 8660 - ionomer   _____

+ PE-620 low density polyethylene   — ·· — ·· — ··

x PE-4005 low density polyethylene   - - - - - - - - - -

[ ]   approximate foaming temperature range

FIG.9

Heat Seal Strength
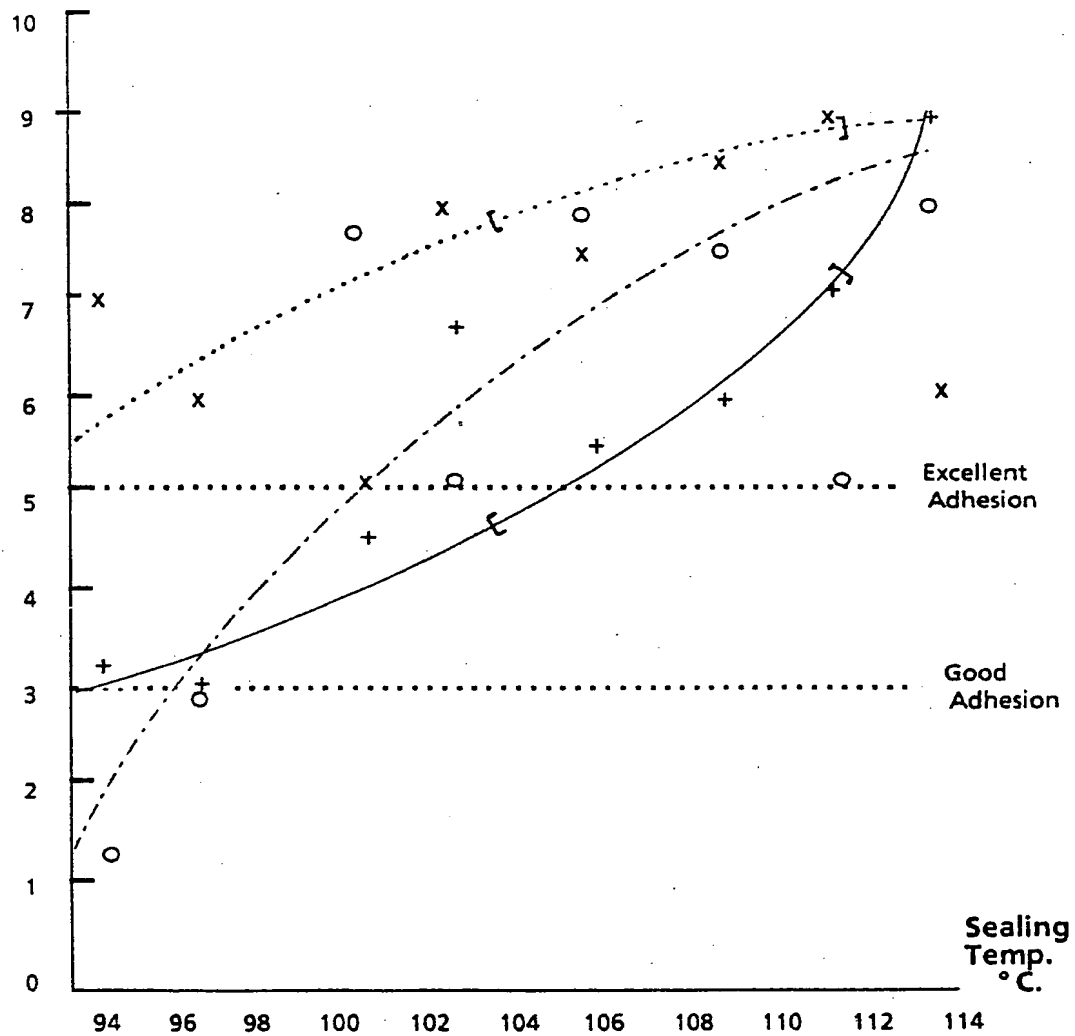(Newtons/ inch width)

Excellent
Adhesion

Good
Adhesion

Sealing
Temp.
° C.
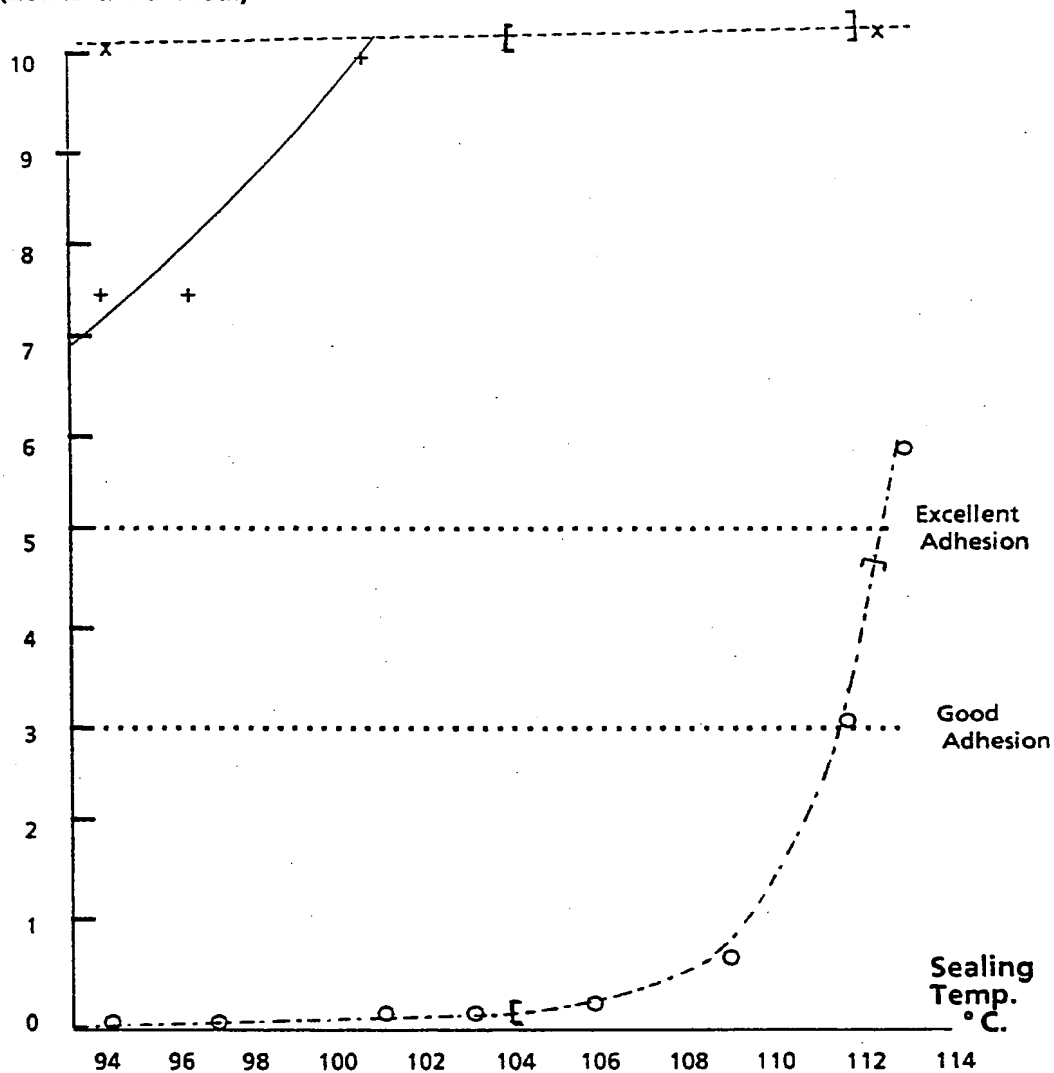
+   PE-620/ EAA 1420 (80:20) —————————

x   PE-620/ EAA 1420 (60:40) ------------

o   PE-620/ PE-4005 (80:20) —·—··—·—··—

[   ]   approximate foaming temperature range

Heat Seal Strength
(Newtons/inch width)

FIG.IO

+   PE-620/ Surlyn 8660 (90:10)   ————————

x   PE-620/ Surlyn 8660 (80:20)   ....

o   PE-4005/ Surlyn 8660 (90:10)   —·—·—·—·—

[   ]   approximate foaming temperature range